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MECHANISMS OF CORROSION FATIGUE OF ALUMINUM ALLOYS.(U)  
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Mechanisms of Corrosion Fatigue  
of Aluminum Alloys

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Abstract

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An overview of experimental variables which are considered critical to understanding the mechanisms of corrosion fatigue of high strength aluminum alloys is presented. Based on this overview, an examination of previously proposed mechanisms is attempted. These models include anodic dissolution, surface energy reduction, and hydrogen embrittlement. It is concluded that hydrogen embrittlement of process zones at alloy surfaces (for crack initiation) and at crack tips (for crack propagation) best explains observed results. A general model of corrosion fatigue of these alloys is proposed. This model suggests that the nature of the naturally formed oxide film on aluminum alloys may be a critical factor. Chemical or mechanical damage of the film allows hydrogen ingress. The presence of second phase particles which may act as sinks for dislocation transported hydrogen, may also be a necessary prerequisite to significant amounts of reduction in fatigue resistance associated with corrosion.

Introduction

It is well known that high strength aluminum alloys are highly susceptible to environmental degradation in the presence of halide ions. In the unstressed state, this degradation may be manifested by localized corrosion such as pitting, crevice corrosion or exfoliation (grain boundary attack). However, under conditions of applied or residual stresses, these alloys may suffer from stress corrosion cracking (SCC) or, if cyclic loads are present, from corrosion fatigue. In some circumstances, these two phenomena may be additive and a form of "stress-corrosion fatigue" may be observed. In general, SCC is reported as time delayed failure of smooth or of notched specimens, often at applied stress levels below the nominal yield strength of the alloy. Alternatively if high aspect ratio flaws such as pre-cracks are present, measurable crack growth may be observed which generally increases with stress intensity ( $K$ ) until a plateau value of crack growth rate ( $da/dN$  or  $a/v$ ) is reached. Both types of data are schematically described in figure 1. Under cyclic loading conditions, similar trends are observed, except that the data which are obtained are generally described as stress ( $S$  or  $\sigma$ ) vs numbers of cycles to failure ( $N_f$ ) on semi-log plots for smooth or notched alloys. For the case of controlled, observable crack growth the data are generally plotted as crack growth increment per cycle ( $da/dN$ ) vs the range of stress intensity ( $\Delta K$ ) (fig. 2). While halide has been shown to significantly increase crack propagation rates (and decrease time to failure) it should be noted that distilled water, and even moist air have been shown to be very effective in inducing environmentally assisted cracking in several high strength aluminum alloys.

Aluminum Alloy Metallurgy

The aluminum alloys which are most seriously affected by environmental degradation of mechanical properties are precisely those of most interest for commercial application i.e. high strength/low density alloys. As a class, they are generally utilized in a precipitation hardened condition obtained by appropriate heat treatment. In general, the precipitates are intermetallic compounds which are formed and distributed as small particles by a solutionizing heat treatment, followed by a quench to maximize the vacancy concentration of the alloy. Aging temperatures and time determine the rate of nucleation and growth, and determine the size, distribution and morphology of the precipitates. The initial G.P. zones are considered to be coherent with the matrix and the final precipitates,  $\eta$ , maintain partial coherency with the matrix (111) plane. (1,2), although as many as seven other matrix/precipitate coherencies have been reported. (1,3) In the peak aged condition slip is considered to be highly planar, while in the underaged or overaged condition slip is generally considered to be more diffuse.

General Fatigue Behavior of High Strength Al Alloys

The fatigue resistance of the more commonly used Al alloys such as 2024 (Al-Cu) and 7075 (Al-Zn-Mg) is considered to be poor when the alloys are tested in the peak hardened

condition. The  $10^7$  cycle fatigue limit in neutral environments is  $\sim 0.3-0.35$  of the UTS, and when cracks form, crack propagation rates are relatively rapid when compared with ferrous alloys. On smooth specimens in the high cycle fatigue regime, or in notched single crystals in inert atmospheres at relatively low stresses, cracks initiate in the stage I (crystallographic) mode and, as in many other alloy systems, convert to a stage II mode at some critical (but as yet undetermined) crack length (for a nominal applied stress below  $\sigma_{ys}$ ). For pre-cracked (fracture mechanics) specimens cracks are generally considered to grow only in the stage II mode. The specific process by which cracks initiate is still somewhat open to interpretation. Several models for crack initiation processes have been proposed and include resolution of ordered precipitates sheared by the slip process (3,4) or, alternatively, disordering of these precipitates thus creating a "soft" region along slip planes where stage I cracking initiates and grows.(5) However, at low applied stresses, approaching the endurance limit, evidence of precipitate by-pass resulting in sessile dislocation loops in the matrix of high purity Al-Zn-Mg alloys has been reported.(6) According to this model the sessile loops generate dilational stresses across slip planes leading to weak planes for crack initiation. It is possible that all of the models may be valid depending on combinations of applied stresses, precipitate morphologies, slip plane orientations etc., and that no simple micro-process can explain all of the observed results.

### Corrosion Fatigue Behavior of High Strength Al Alloys

#### A. Gaseous Environments

Corrosion fatigue of precipitation hardened Al alloys has been observed in environments as innocuous as damp laboratory air. In general, this environment has little or no effect on crack initiation processes, but reductions in the general S-N behavior have been reported. Additionally, crack propagation experiments indicate significant increases in  $da/dN$  for a given  $\Delta K$ .(7,8)(fig.3) In order to observe a significant effect, water vapor must be present in the environment, oxygen alone having little or no effect on either fatigue lives or fatigue crack propagation rates.(9) In fact, virtually identical crack propagation rates have been observed for a 7075 type alloy in wet argon, wet oxygen and wet air.(7) While the presence of some water vapor is important, increases in water vapor concentrations in air do not increase crack propagation rates significantly when a critical concentration of water vapor has been exceeded.(8) The water vapor effect has been linked to a form of hydrogen embrittlement (9,10), although gaseous hydrogen does not appreciably affect fatigue resistance.

Water vapor has also been shown to affect crack paths in single crystals of an Al-Zn-Mg alloy. In dry air for a peak hardened alloy, conventional stage I cracking in {111} planes was observed, but exposure to moist air increased crack propagation rates and cracks grew in {100} planes.(11,12) The effect is frequency sensitive and no appreciable effect is observed at 50 Hz, although a marked effect is noted at 5 Hz.(12) Also, a test started 50 Hz but switched to 5 Hz alters the crack path out of the slip band; but a test began at 5 Hz and switched to 50 Hz does not move the crack path back to the slip band.(fig. 4) These results indicate that the effect is time dependent and that the process is a bulk alloy effect, rather than simply being strictly a surface related effect. In other experiments Wei and his co-workers have convincingly confirmed that the effect is in fact a bulk effect, but that the rate limiting step is not necessarily diffusion. Rather it appears to be related to a surface reaction of the water vapor on the aluminum alloy fracture surface which releases the damaging specie, presumed to be hydrogen.(10,13)

The specific process by which hydrogen embrittles the alloy under cyclic deformation conditions is still open to question and most of the "classical" hydrogen cracking models have been invoked. These include high internal pressures at voids or defects in the alloy (14), surface energy reduction by the embrittling specie due to adsorption (15-17), effects of slip reversibility (18) and changes in the mechanical properties of the oxide film.(19) The high internal pressure theory suggests that hydrogen preferentially diffuses to regions of high hydrostatic stress ahead of a growing crack, precipitates, and increases the local tensile forces during the crack advance. Adsorption effects are thought to lower the surface energy required to create new crack surfaces, although the energy associated with crack tip plasticity is generally ignored. Hydrogen or other surface reactive species may also affect surface slip reversibility or alternatively crack tip plasticity resulting in less crack blunting as the crack surfaces are unloaded.

#### B. Aqueous Environments

While the previously cited results of the effects of gaseous environments are relatively recent, severe corrosion fatigue of Al alloys in aqueous, particularly saline, environments has been recognized for some time. Some of the earliest observations indicated that, for Al-Zn-Mg alloys, fracture surface appearance showed distinct differences when saline environments and dry air were compared.(20,21) Specifically "ductile" striations (type "A") were observed in dry air, while "brittle" striations (type "B") were observed to occur in the saline solutions. Examples of these two morphologies are shown in Fig. 5. The type "A" striations were observed to be non-crystallographic and showed extensive shear, while type "B" striations were identified as occurring on or near {100} planes.

It has also been observed that crack propagation rates were typically 3-10X more rapid in aqueous environments when compared to dry air.(10,22) Also it has been reported that, the more aggressive is the solution toward general corrosion of the aluminum alloys, the lower is fatigue resistance when tested in those environments. Thus increasing ionic concentration, particularly of halides, and both acid and basic solutions (where corrosion rates of aluminum increase) decrease fatigue resistance.(23) Lowering the corrosive nature of the solutions by adding inhibitors, such as nitrates, conversely increases the fatigue resistance.(17) However, it has been shown that cathodic polarization of the alloy, (cathodic protection) may actually decrease fatigue resistance in nominally neutral solutions.(fig. 6) Anodic polarization, which invariably increases corrosion rates virtually always results in a degradation in fatigue resistance.(23,24) The general consensus of experiments utilizing polarization as a variable, are that small amounts of cathodic polarization slightly increase fatigue resistance but that large amounts of polarization lead to decreases in fatigue resistance. These results are by no means unequivocal, however. When significant amounts of cathodic polarization are applied, the evolution of hydrogen at the alloy surface results in a shift in the solution pH in the positive direction, and basic solutions are known to be corrosive to aluminum alloys. Additionally, the aqueous solution in growing cracks is quite different from the bulk solution and, in some cases, may be quite independent of surface polarization.(25,26)

A recent experimental program in our laboratories has been specifically addressed toward understanding the mechanism of corrosion fatigue in a 7075 alloy and its high purity Al-Zn-Mg-Cu analogue. A summary of the results of this program follows.

1) It has been shown that  $\text{Cl}^-$  ion is not a prerequisite to induce lowered fatigue resistance in either alloy, particularly under conditions of cathodic polarization. Sulfate ion, while less damaging under free corrosion conditions, is equally aggressive at equivalent cathodic potentials. In chloride solutions under freely corroding conditions, surface pits dominate the crack nucleation event, but fatigue resistance in sulfate solutions where pitting is not observed is equivalent to that observed in distilled water.(fig. 2,7)

2) In distilled water or in sulfate solutions, under free corrosion conditions, only ductile situations are observed on the fracture surfaces, versus brittle situations invariably observed in chloride solutions. Under cathodic polarization conditions brittle situations are observed on all fracture surfaces.

3) Pre-corrosion experiments in NaCl followed by tests in laboratory air result in significant decreases in fatigue resistance. However, this effect is at least partially reversible. Post exposure heat treatments prior to fatigue testing increase fatigue resistance with larger increases observed as heat treatment times are extended.(Table I)

4) In aggressive environments, the cyclic stress is the primary mechanical factor controlling the fatigue resistance. The magnitude of mean stress is only of secondary importance.(fig. 8)

5) Corrosion fatigue resistance of aluminum alloys is less sensitive to Mode III (torsional) loading than to Mode I (tensional) loading.(fig. 9)

6) Heat treatments which improve SCC resistance, (eg.T73) have little or no effect on corrosion fatigue behavior in  $\text{Cl}^-$  solutions.

#### Specific Mechanisms of Corrosion Fatigue of Al Alloys

As already briefly mentioned, there are at least three principal mechanisms which have been suggested to explain the reduction of fatigue lives in Al alloys exposed to aggressive environments.

##### A. Strain Enhanced Dissolution

Older versions of this mechanism suggested that strained atomic bonds are more likely to lead to atomic dissolution (corrosion) than are unstrained bonds. Refinements to the mechanism include the role of plastic strain associated with dislocations intersecting the free surface of a metal or alloy during fatigue, resulting in preferential attack of emerging slip bands.(27) It has also been suggested that this preferential attack accelerates further slip processes in a kind of autocatalytic process. Evidence for such a model has been shown for mild steels and for copper alloys under controlled corrosion conditions.(28-30) It has also been shown that if corrosion rates are sufficiently low, fatigue resistance is unaffected by the environment. Another version of the strain assisted dissolution model is the film rupture theory. According to this mechanism, mechanical rupture of an otherwise protective film leads to rapid localized corrosion at the film rupture site, leading to crack initiation in emerging slip bands, and subsequently to corrosion assisted crack growth due to the high stress concentrations associated with crack tips.(24,31-36)

While these mechanism can be used to explain results observed for aluminum alloys exposed to liquid phase corrosive solutions, it is difficult to relate them to the significant decreases in fatigue resistance observed in water vapor or in degassed distilled water. Additionally, the observation that the effects of pre-corrosion are at least partially reversible through conventional heat treatments suggests that this mechanism may be untenable even for aqueous corrosion fatigue. Thus, it may be considered that strain assisted dissolution processes cannot adequately explain either crack initiation

processes or enhanced crack propagation process for these alloys.

### B. Surface Energy Reductions

According to this theory, specific species which are strongly adsorbed at surfaces serve to lower the local bond energy and accordingly lead to increases in crack propagation rates. Some investigators have also suggested that reductions in surface energy may enhance plasticity and cause early crack initiation and propagation.(37) Still other investigators have suggested that surface energy reductions in growing cracks may reduce crack tip plasticity and thus induce brittleness.(17) Problems with acceptance of adsorption models have generally centered on the large amount of plastic energy associated with crack growth vs the relatively small amount of surface energy ( $\sim 10^3$ ). Thus even large changes in surface energy should not appreciably affect cracking tendencies. Also, the observation that  $\text{SO}_4^{2-}$  ion is at least as damaging as  $\text{Cl}^-$  ion under cathodic charging conditions would tend to discount a specific species explanation.

### C. Hydrogen Assisted Cracking

The possibility that aluminum alloys may suffer from hydrogen embrittlement was strongly suggested by experiments which showed that, for thin specimens, air borne water vapor caused totally brittle failures in Al-Zn-Mg alloys.(38,39) In fact, brittle intergranular cracks were observed by high voltage transmission electron microscopy in thin foils of these alloys with no signs of anodic dissolution or plasticity. Further experiments indicated that, after exposure of this alloy to water vapor, voids were observed to grow from interactions with a focused electron beam. Also, fracture of these specimens in a mass spectrometer was accompanied with the release of clearly identifiable amounts of hydrogen.(39) Tensile experiments in an Al-Mg alloy (5086) charged with tritium also showed discontinuous yielding associated with tritium release.(40) It appears certain then, that Al alloys which contain hydrogen are accordingly embrittled and that there appears to be a dislocation - hydrogen interactions.

### Proposed Mechanism of Corrosion Fatigue of Al Alloys

On the basis of the results presented in this discussion, and on recently obtained but yet unpublished results obtained at Rensselaer, it appears that this latter mechanism, that of hydrogen embrittlement, can successfully be applied to corrosion fatigue of high strength aluminum alloys. Table II summarizes some of the relevant arguments with support or lack of support for either a hydrogen embrittlement process or an anodic dissolution process. Perhaps the most significant observations are that water vapor alone can produce increases in crack propagation rates, which are equivalent to increases in rates obtained in distilled  $\text{H}_2\text{O}$  alone or with  $\text{Na}_2\text{SO}_4$  additions. Also, the partial reversibility of damage when tested in air after exposure to pre-corrosion is strongly indicative of a dissolved species rather than an adsorbed species which is responsible for embrittlement. Other peripheral observations such as the effects of load mode (Mode I or tension being worse than Mode III or torsion) and the absence of mean stress effects permit the presentation of a qualitative model for corrosion fatigue of high strength Al alloys. According to this model hydrogen, dissolved in the alloy, in the process zone at a crack tip, embrittles this region and causes increases in crack propagation rates. The specific process by which the embrittlement occurs remains elusive, although it may be significant that those alloys which have small, semi-coherent particles are the most susceptible to failure. Consideration that the non-coherent precipitate-matrix interface at grain boundaries in statically loaded specimens is the preferred crack path, suggests that hydrogen may collect at these interfaces to cause decohesion. Under cyclic loading conditions, the mobile dislocations may act as short circuit paths for hydrogen to precipitate at interfaces in the grain interiors in preference to grain boundary regions. Thus the fracture path is shifted to transgranular, since effective diffusion rates are enhanced still more than are grain boundary diffusion rates. It may be significant to note that, for alloys with equiaxed grains, low cyclic stresses and small amounts of cathodic charging result in intergranular crack initiation and early propagation even under cyclic loading conditions. As the cracks elongate however, the local effective stress increases, dislocation densities and mobilities increase, and the cracks shift to a transgranular mode.(Table III) The crack path shift to  $\{110\}$  or  $\{112\}$  planes from the  $\{111\}$  slip planes (in non-aqueous environments) which has been reported may also be associated with a particular precipitate/matrix interfacial plane where hydrogen collects. Since it has also been shown that sulfate is as effective as chloride in reducing fatigue resistance if external sources of hydrogen, (cathodic charging) are applied, the specific role of chloride appears to be related to chemical damage of the otherwise protective film allowing the ingress of hydrogen to the alloy. In the absence of chemical damage to the film, mechanical damage by slip step intersection, first with the free surface for crack initiation, and subsequently with advancing fracture surfaces, allows hydrogen to enter the alloy, again presumably carried by dislocations. Thus non-chloride containing aqueous media (water vapor, distilled water,  $\text{SO}_4^{2-}$  solution, etc.) all behave in a similar manner. According

to this model, only the process zone at the crack tip need contain hydrogen to cause accelerated crack growth. Thus the normally low bulk diffusion rates generally reported for hydrogen in aluminum alloys need not be rate controlling.

A second aspect of the model is the requirement for a specific distribution and morphology of strengthening precipitates. Thus alloys such as 1100 Al (commercially pure) or 2024 (Al-Cu) would not necessarily be expected to be embrittled. Likewise, overaging or underaging heat treatments which alter precipitate/matrix relationships would be expected to alter the sensitivity of alloys to corrosion fatigue.

In summary, the key to the corrosion fatigue phenomenon in Al alloys may be related to the method by which hydrogen enters the alloy. Since the naturally formed film on the alloy appears to exhibit a low permeation to hydrogen, those mechanical or chemical events which weaken or damage the film may control the crack initiation/propagation process. This would then help to explain the effects of cyclic stress range and the lack of effect of mean stress level (mechanical factors) and the effects of such variables as chloride ion, high or low pH, applied potentials or currents, and solution chemistry in general.

#### Summary

To summarize, a model for corrosion fatigue of high strength Al alloys is proposed which is dependent on surface film integrity. Chemical or mechanical damage to the film, allowing exposure of hydrogen to emerging dislocations (slip planes) which effectively "pump" hydrogen into the crack process zone. It is further suggested that the hydrogen collects at precipitate matrix interfaces and, through some still unknown specific mechanism, causes separation of the interfaces. The model is an extension of previous models proposed for stress corrosion cracking of these alloys, except that the cyclic nature of the dislocation motion creates a preferentially high diffusion path into the process zone rather than into the normal high diffusivity zone of grain boundaries.

#### References

1. J.T. Staley: Met. Eng. Quarterly, 1976, vol. 16, p. 52.
2. C.E. Lyman and J.B. VanderSande: Met. Trans., 1976, vol. 7A, p. 1211.
3. P.J.E. Forsyth, Acta Met., 1963, 11, 703.
4. C.A. Stubbington and P.J.E. Forsyth, J. Inst. Metals, 1961, 90, 374.
5. Calabrese, C. and Laird, C., The cyclic stress-strain response of metals and alloys, Proc. 3rd Int. Conf. on Fracture, Munich, 1973, Vol. 6, V231; Cyclic stress-strain response of two-phase alloys, I. Microstructures containing particles penetrable by dislocations, II. Particles not penetrable by dislocations, Mater. Sci. Eng., 13, 141, 1974.
6. D.J. Duquette and P. R. Swann, Acta Met., 1976, 24, 241.
7. A. Hartman: Int. J. of Fract. Mech., 1965, vol. 1, p. 167.
8. P.P. Wei: Eng. Fract. Mech., 1970, vol. 1, p. 533.
9. T. Broom and A. Nicholson: J. Inst. of Metals, 1960, vol. 89, p. 183.
10. R.P. Wei: Int. J. of Fract. Mech., 1968, vol. 4, p. 159.
11. M. Nageswararao, G. Kralik and V. Gerold: Z. Metallik, 1975, vol. 66, p. 479.
12. M. Nageswararao and V. Gerold: Met. Trans., 1976, vol. 7A, p. 1847.
13. G.J. Hudak and R.P. Wei: Corrosion Fatigue ed. O. Devereux, A.J. McEvily and R.W. Staehle, 1971, p. 433, NACE, Houston.
14. C. Jaffe and C. Sims, Trans. Met. Soc. AIME, (1941), 145, 225.
15. R.M. Pelloux: Fracture 1962, op. cit., p. 731.
16. R.J. Delines and R.M. Pelloux: Met. Trans., 1972, vol. 3, p. 2525.
17. R.E. Stoltz and R.M. Pelloux: Met. Trans., 1972, vol. 3, p. 2433.
18. R.M.M. Pelloux: Adv. Trans. Quart., 1969, vol. 62, p. 281.
19. J.C. Grosskreutz: Surface Sci., 1967, vol. 8, p. 173.



20. C.A. Stubbington, Metallurgia, 1963, vol. 65, p. 109.
21. P.J.E. Forsyth: Acta Met., 1963, vol. 11, p. 703.
22. R.P. Wei and J.D. Landes: Int. J. of Fract. Mech., 1969, vol. 5, p.69.
23. R.J. Jacko, Ph.D. Thesis, Rensselaer Polytechnic Institute, (1978).
24. F.P. Ford: Ph.D. Thesis, Cambridge University, 1973.
25. B.F. Brown, C.T. Fujii and E.P. Dahberg: J. Electrochem. Soc., 1969, vol. 116, p. 218.
26. A.J. Sedricks, J.A.S. Green and D.L. Novak: Localized Corrosion, op cit., p. 569.
27. D. Whitwham and U.R. Evans: J. Iron and Steel Inst., 1950, vol. 165, p. 72.
28. D.J. Duquette and H.H. Uhlig, Trans. ASM, (1968), 61, 449.
29. D.J. Duquette and H.H. Uhlig, Trans. ASM, (1969), 62, 329.
30. H.N. Hahn and D.J. Duquette, Acta Met., (1978), 26, 279.
31. K. Laute: Oberflächentech, 1933, vol. 10, p. 281.
32. T. Pyle, V. Rollins and D. Howard: Corrosion Fatigue: Chemistry, Mechanics and Microstructure, op. cit., p. 312.
33. T. Pyle, V. Rollins and D. Howard: J. Electrochem. Soc., 1975, vol. 122, p. 1445.
34. C. Patel, T. Pyle and V. Rollins: Met. Sci., 1977, vol. 11, p. 185.
35. C. Patel, T. Pyle and V. Rollins: Nature, 1977, vol. 266, p. 517.
36. F.P. Ford and T.P. Hoar: Proc. of 3rd Int. Conf. on Strengthening of Metals and Alloys, Cambridge, 1973, paper 95.
37. S.P. Lynch: in Mechanisms of Environment Sensitive Cracking of Materials, 1977, p. 201, The Metals Society, London.
33. G.M. Scamans and C.D.S. Tuck: Second Int. Cong. on Hydrogen in Metals, Paris, 1977, paper 4A11.
39. L. Montgrain and P.R. Swann: Hydrogen in Metals, op. cit., p. 575.
40. J.A. Donovan: Met. Trans., 1976, vol. 7A, p. 1677.

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TABLE I

The Effect of a Re-Heat Treatment Duration on Subsequent Fatigue

Properties in Air

Pre-Corrosion: 24 hours in aerated 0.5 NaCl

Re-heat treat: Solutionize at 470°C for x hours  
Age at 121°C for 24 hours

Fatigue in air: Mean stress 276 MPa, Cyclic Stress  $\pm$  96 MPa

<u>Time at 470°C</u>	<u>N<sub>f</sub></u>
0 hours	30,000 cycles
3 hours	85,000 cycles
6 hours	101,000 cycles
24 hours	> 13,000,000 cycles

TABLE II

Effect of Cyclic Load on the Fracture

Morphology of Al-5.5Zn-2.5Mg-1.5Cu

in 0.5M NaCl Polarized to -1.75V vs. SCE

<u>Cyclic Stress MN/m<sup>2</sup></u> <u>at <math>\sigma_m = 207</math> MN/m<sup>2</sup></u>	<u>% Intergranular Failure</u>
76	0
69	0
55	0
41	10
28	26
17	35

TABLE III

A Summary of Experimental Observations on the Mechanisms of Corrosion Fatigue  
of Al Alloys

<u>Experimental Observation</u>	<u>Hydrogen Embrittlement</u>	<u>Enhanced Anodic Dissolution</u>
Sensitivity to water in both the liquid and vapor form.	Strong support for H.E.	Water vapor should have no effect when crack is not filled with a liquid phase.
Crack path shift reported from {111} to {100} in aggressive solutions.	Consistent with environmentally induced cleavage.	Not easily attributable.
Sensitivity to Anion Type and Concentration.	Affects the passivation rate and oxide film stability which control both mechanisms.	
Decreased fatigue resistance in both acid and basic $\text{Na}_2\text{SO}_4$ .	Consistent if modifications in the oxide are more important than $\text{H}^+$ concentration of bulk solution.	Supportive because both make the oxide less stable and make dissolution easier.
Decreased fatigue resistance with cathodic polarization in NaCl.	Supportive, higher surface hydrogen concentration.	Some support, can be explained by changes in oxide film.
Decreased fatigue resistance with anodic polarization in NaCl.	Consistent with the imp-protective nature of oxide and higher $\text{H}^+$ activity.	Supportive, increasing dissolution rate increases rate of cracking.
Decreased fatigue resistance in $\text{Na}_2\text{SO}_4$ with cathodic polarization.	Parallel behavior as in NaCl because there is increased hydrogen in both solutions.	Some support due to less protective oxide film.
Similarity between potential dependence for fatigue and hydrogen permeation in NaCl.	Strong support.	Can be explained by modifications in oxide film behavior.
Fatigue in deaerated solutions.	Consistent with easier H entry.	Can be explained by resultant changes in the oxide film.
Pre-exposure effect and the partial reversibility upon re-heat treatment.	Unambiguous support for H.E.	Cannot be explained.
Insensitivity of fatigue lives to mean stress in aggressive environments.	Consistent with idea of H transport by mobile dislocation which are produced by cyclic stress component.	Consistent with mechanism because the cyclic stress controls the slip step area exposed.
Insensitivity to aggressive environments under Mode III loading compared to Mode I loading.	Supportive, there is no hydrostatic stress component in Mode III to concentrate H in the crack tip region.	Not supportive unless effect is due to the inability of the solution to get to the crack tip region. This is considered unlikely in the dynamic fatigue testing.

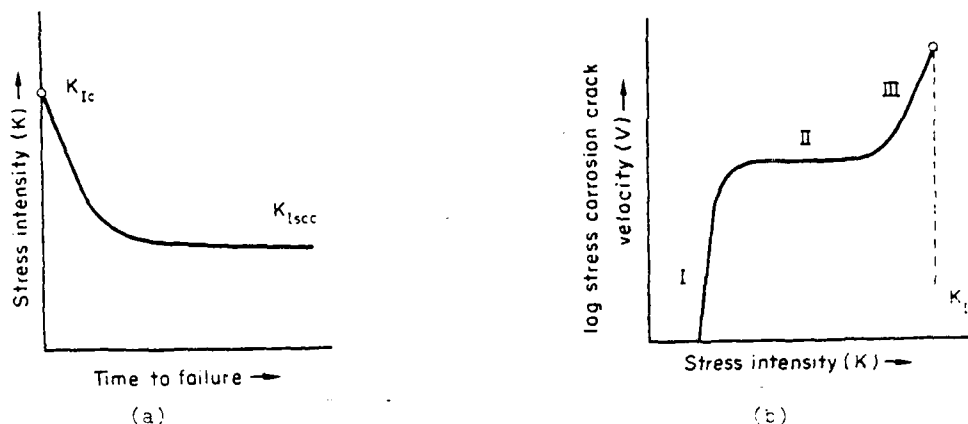


Figure 1. a) Schematic diagram of stress intensity factor ( $K$ ) versus time to failure in a stress corrosion environment at  $K$ . Below  $K_{Isc}$  failure should not be observed. This type of data is also reported as stress versus  $K_{Isc}$  time to failure for smooth specimens, and a threshold stress level is then determined.

b) Schematic diagram of crack velocity versus stress intensity factor for an alloy susceptible to SCC.  $K_{Isc}$  is often described by the intersection of stage I cracking with the  $K$  axis. Stage III cracking is not always observed and  $K_{Ic}$  is the fracture toughness of the alloy in the absence of environment.

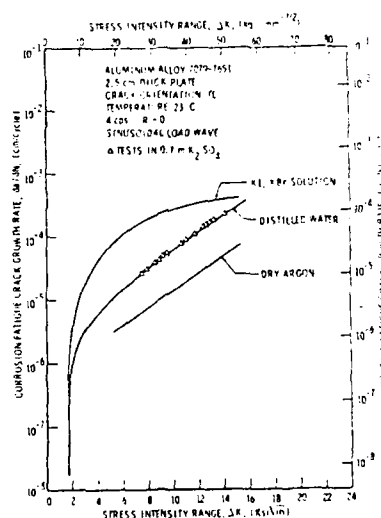


Figure 2.

Figure 2. Typical fatigue crack propagation data for a precipitation hardened aluminum alloy. It should be noted that crack propagation rates in distilled water and in 0.7 M  $K_2SO_4$  are identical and greater than in argon but that halides considerably increase crack propagation rates at virtually all  $\Delta K$  values.

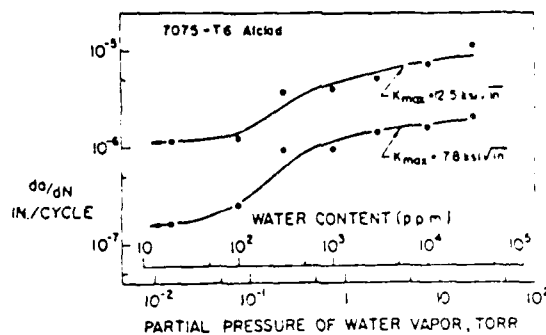
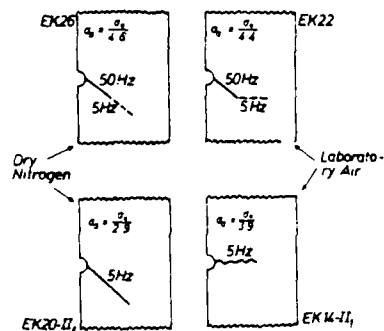


Figure 3.

Figure 3. Typical crack propagation data for a precipitation hardened aluminum alloy as a function of the partial pressure of water vapor. Note that the behavior is similar for each  $K_{max}$  value, but that there is a marked increase in crack propagation rates at  $p_{H_2O} > 10^{-1}$  torr. With the exception of the transition zone between  $10^{-1}$  and  $10^0$  torr  $da/dN$  is virtually constant.



(a)

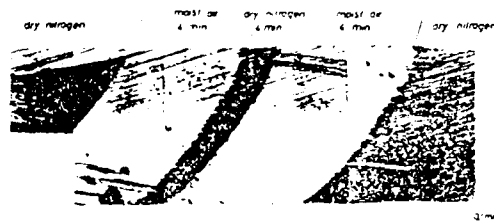


Figure 4. a) Schematic diagram of crack propagation in high purity Al-Zn-Mg alloy single crystals exposed to dry  $N_2$  and to laboratory air (with some unmeasured water vapor present) as a function of frequency. In  $N_2$  cracks grow crystallographically independent of test frequency. However, in air, decreasing test frequency either causes the crack to deviate to a stage II mode or, if the test is begun at a low frequency, the stage I mode is not observed. These data suggest a time dependent reaction in laboratory air.

b) Fracture surface of an Al-Zn-Mg single crystal showing that, at a constant frequency, crack propagation rates are considerably increased in moist air vs. in dry  $N_2$ .

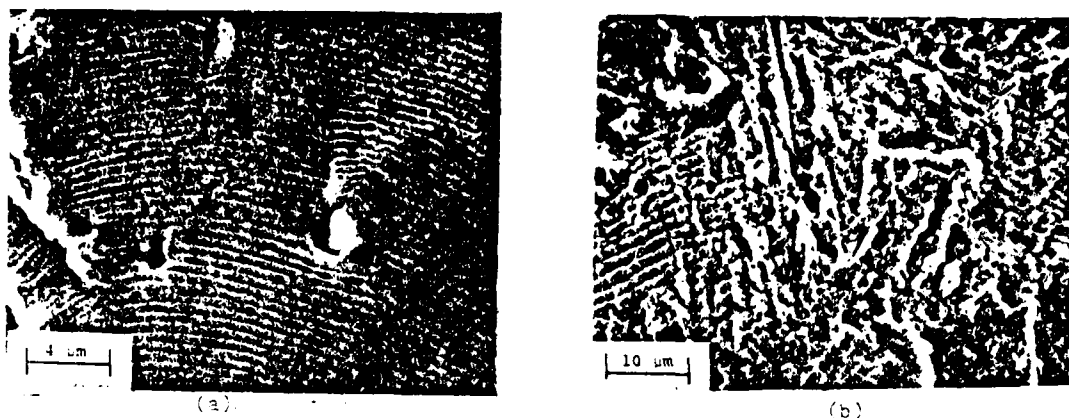


Figure 5. Fatigue fracture surfaces of 7075 T6 tested in (a) dry air showing ductile or type A striations and (b) in 0.5 NaCl showing brittle or type B striations. Tests of this alloy in distilled water or in 0.5 M  $\text{Na}_2\text{SO}_4$  produce striations similar to type A but the application of cathodic potentials in  $\text{Na}_2\text{SO}_4$  causes a change to type B. Arrows indicate direction of crack growth and brackets indicate crack advance per cycle.

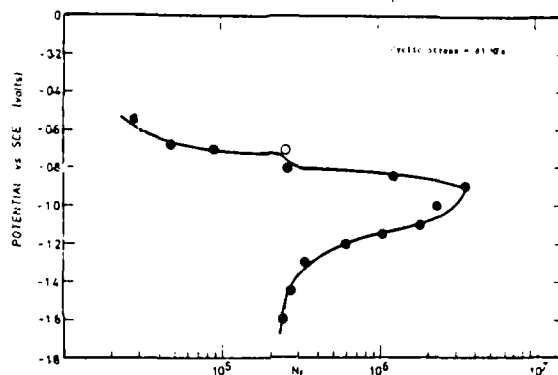


Figure 6.

Figure 6. Fatigue life versus electrochemical potential for a 7075-T6 alloy in 0.5 M NaCl. The open circle corresponds to the corrosion potential. Small cathodic potentials increase fatigue lives, but larger deviations for the corrosion potential cause a decrease in fatigue resistance. Anodic polarization always decreases fatigue resistance.

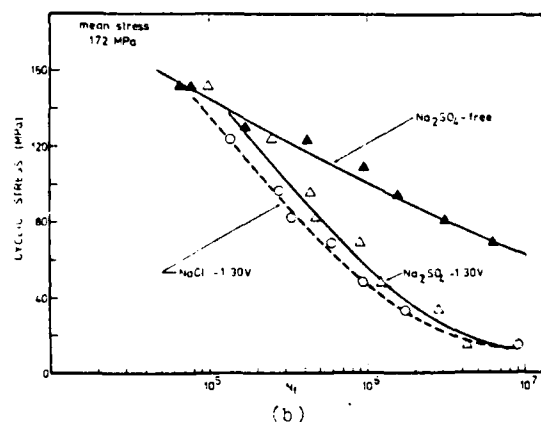
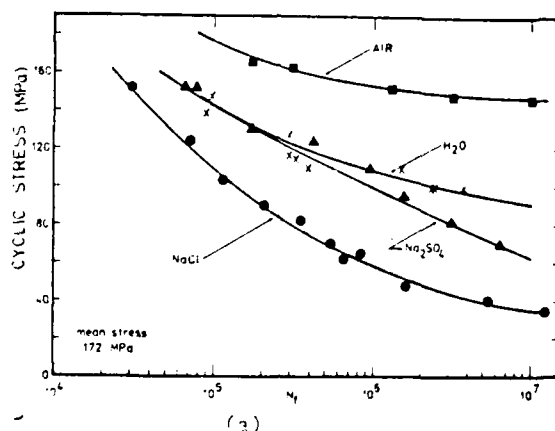


Figure 7. (a) Fatigue behavior of 7075-T6 exposed to air,  $\text{H}_2\text{O}$  and 0.5 M  $\text{Na}_2\text{SO}_4$  and 0.5 M NaCl.  $\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  solutions show similar behavior (see Figure 2).

(b) Effect of cathodic polarization of 7075-T6 in 0.5 M NaCl and 0.5 M  $\text{Na}_2\text{SO}_4$  showing essentially identical behavior for either anion.

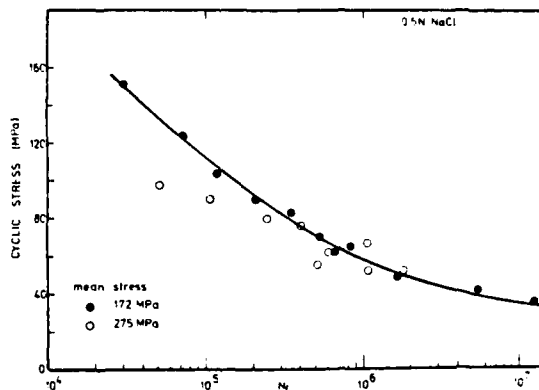


Figure 3.

Figure 3. Effect of mean stress on the corrosion fatigue behavior of 7075-T6 in 0.5 N NaCl solution showing that, except at very large cyclic stresses (above  $\sigma_{ys}$ ) mean stress has virtually no effect on fatigue resistance.

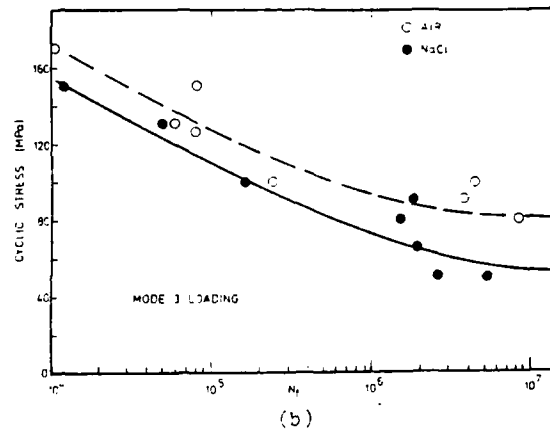
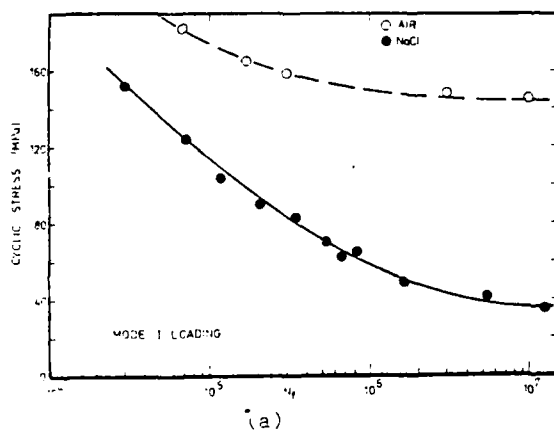


Figure 2. The effect of loading mode on fatigue resistance of 7075-T6 in 0.5 N NaCl solution. These data show that loading in shear has little effect on corrosion fatigue susceptibility when compared with tensile loading. The slight decrease in resistance which is observed in Mode III loading can probably be explained by the non-isotropic nature of the alloy.

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13. ABSTRACT An overview of experimental variables which are considered critical to understanding the mechanisms of corrosion fatigue of high strength aluminum alloys is presented. Based on this overview, an examination of previously proposed mechanisms is attempted. These models include anodic dissolution, surface energy reduction, and hydrogen embrittlement. It is concluded that hydrogen embrittlement of process zones at alloy surfaces (for crack initiation) and at crack tips (for crack propagation) best explains observed results. A general model of corrosion fatigue of these alloys is proposed. This model suggests that the nature of the naturally formed oxide film on aluminum alloys may be a critical factor. Chemical or mechanical damage of the film allows hydrogen ingress. The presence of second phase particles which may act as sinks for dislocation transported hydrogen, may also be a necessary prerequisite to significant amounts of reduction in fatigue resistance associated with corrosion.		

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